# Temperature & Solvent effects on the anodic oxide films formed on Zr-Nb in 0.1M EDTA (sodium salt): Scanned electron micrograph studies.

**[1]V. Jeevana Jyothi , [2]Ch. Anjaneyulu**
[1]Associate Professor, [2]Retd. Professor
[1]Dept. of Chemistry, [2]Department of Chemistry
RBVRR Women's College, Osmania University, Hyderabad, Telangana, India
Email: [1] jeevana.j@rediffmail.com

***Abstract:*** *Anodization of Zr-Nb in 0.1M EDTA (Sodium salt) has been carried out. Kinetics of anodic oxidation of Zr-Nb has been studied at a constant current density of 8mA.cm$^{-2}$and at room temperature. The plots of formation voltage vs. time, reciprocal capacitance vs. time and reciprocal capacitance vs. formation voltage were drawn. From these plots, formation rate, current efficiency and differential field were calculated. The Addition of Solvent (Ethylene glycol) showed better kinetic results. For 20%, 40%, 60% and 80% aquo-glycolic media, the dielectric constant values are low leading to the marked improvement in the kinetics. The surface morphology of the anodic films was also studied by Scanning Electron Micrographs (SEM). Kinetics was also studied at different temperatures ranging from 273K to 333K at a constant current density of 8 mA.cm$^{-2}$. It was observed that kinetic results were found to be increasing linearly with the decrease in temperature*

***Key Words:*** *Anodization, formation rate, current efficiency, differential field, Zr-Nb, EDTA (Sodium salt), Temperature*

## 1. INTRODUCTION:

Zirconium based alloys are used as the structural material in the water cooled thermal reactors [1, 2]. Zr-Nb, due to their low cross-section for thermal neutrons and because of their relatively good corrosion resistance against water and steam, used in water cooled reactors. Zirconium & its alloys are of primary importance in nuclear technology. Anodization of Zirconium alloys have been studied in some electrolytes [3-6]

In the present work, the kinetics of anodic oxidation of Zr-Nb in aqueous solutions of 0.1M EDTA (sodium salt) and aquo-glycolic media in various proportions (v/v) of water-ethylene glycol mixtures ranging from 0% to 80% ethylene glycol are studied. Scanning electron microscopic studies was also carried out to observe the changes in the surface morphology of the anodic films formed.

Kinetics was also studied at different temperatures ranging from 273K to 333K at a constant current density of 8 mA.cm$^{-2}$.

## 2. LITERATURE SURVEY:

Vermilyea studied the formation of anodic films on tantalum in aqueous [7] and non-aqueous [8] solutions. He suggested that the composition of film depends on the solution in which it is formed.

Seregina et al [9] studied the anodization of aluminium alloys in the solution of sulpho-salicylic acid (90g/cc) and found that thick films are possible during anodization at room temperature. Nageshwar rao et al [10] observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic

Aparna [11] also observed the same trend of increasing kinetic results with increase in glycol content in 0.1M Picolinic acid and sodium methoxide for Zr-2 and Ti. Vermilyea [8] reported that the optical thickness was smaller in the non-aqueous solutions, and the increase in weight for a given charge passed could be as much as twice that expected.

Moshashi Koyama [12] carried out anodization of titanium in non-aqueous media and confirmed that the oxide film consists of double layers and suitable for electrolytic capacitors. Wei Wei et al [13] reported the growth of layers by anodization of tantalum in a non-aqueous electrolyte consisting of an optimized glycerol/ethylene glycol mixture with the addition of $NH_4F$

Schmidt et al [14] observed that the layers of $TiO_2$ obtained in non-aqueous electrolytes are much adherent and uniform than those realized in aqueous media. Climent Montoliu et al [15] studied the anodization of titanium in acid, alkali and neutral baths (aqueous and aquo-glycolic) and suggested from the structure and dielectric properties, that the anodic coatings formed in non-aqueous media acts as better dielectric capacitors.

Panasa Reddy et al [16] and Lavanya et al [17] also studied in trisodium citrate, 0.1M KOH (aquo-glycolic) respectively and found that the breakdown voltage was higher when anodized in ethylene glycol medium. This was also supported by other workers [18]. Shukla [19] carried out the study of effect of aquo-glycolic media on Anodization of zircaloy-4 in 0.1M sulphamic acid and found that the addition of solvent improved the kinetic results.

## 3. MATERIALS:

Zr-Nb was of 98% nominal purity, supplied in the form of annealed rolled sheet with 0.2mm thickness, supplied by Nuclear Fuel complex, Hyderabad as gift samples. A typical composition of nuclear-grade zirconium alloys is more than 95 weight percent zirconium and less than 2% of tin, niobium, iron, chromium, nickel and other metals, which are added to improve mechanical properties and corrosion resistance

In the present work, the foil samples used were cut with the aid of a punch into flag-shaped specimens of $1cm^2$ working area on both sides and 2cm long tag. The chemical polishing mixture consisted of acids such as $HNO_3$, $H_2O$ & HF in a definite volume ratio of 3:3:1.

Electrolytes used were 0.1M EDTA (sodium salt) in 20%, 40%, 60% and 80% aquo-glycolic mixtures, the solvent being ethylene-glycol. The temperatures used in the current study were ranging from 273K to 333K by using a Thermostat

## 4. METHODS:

For anodizing, a closed shell of 200ml capacity was used. The cathode used was a platinum foil of $20cm^2$ superficial area to make double layer capacitance as large as possible.

All the experiments were carried out at a constant current density of $8mA.cm^{-2}$.The experimental procedure for the anodization is given elsewhere [20]. The kinetic results calculated are formation rate in $Vs^{-1}$, current efficiency (ɳ) % and differential fields of formation ($F_D$) in MV $cm^{-1}$ from the conventional plots V vs. t, 1/C vs. t and 1/C vs. V.

The Kinetics of film formation was studied at different concentrations of added solvent i.e Ethylene glycol to the main electrolyte. The temperatures used in the current study were ranging from 273K to 333K by using a thermostat.

The surface morphology of the anodic film was examined using Scanning Electron Microscope (SEM). The SEM's were taken at IICT-CSIR, Hyderabad.

The surface was thoroughly rinsed with distilled water and dried under infrared lamp and cleaned gently with fine tissue paper. The surface was coated with gold, palladium conducting material using evaporation technique and signal processed secondary electron images were taken from scanning electron microscope model SEM Hitachi- S520 at 10 KV, Hitachi instruments made in Japan (Oxford link ISIS- 300 UK)

## 5. RESULTS & DISCUSSIONS:

Anodization of Zr-Nb was done in 0.1M EDTA (Sodium salt). The formation rate, current efficiency and differential field were calculated. The effect of solvent and temperature on Zr-Nb was studied in 0.1M EDTA (Sodium salt) to check whether there was enhancement in kinetics of film formation [21, 22].

### 5.1 EFFECT OF SOLVENT:

Anodization of Zr-Nb in 0.1M EDTA (Sodium salt) was performed by mixing various proportions of ethylene glycol to the aqueous solution (20%, 40%, 60% and 80%). There was an improvement in the kinetics as given in Table-1. The relevant plots are shown in Figures-1 & 2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors [23]. These facts support the current results obtained in aquo-organic mixtures of 0.1M EDTA (Sodium salt). It can be explained on the basis of decrease in the dielectric constant of the medium (Table-2)

In solutions of low dielectric constant there is less chance of ion-dipole interactions (solvent-ion interactions) which do not interfere in the oxide film formation. However, the ions in the high dielectric constant solutions interact with oxide ions responsible for oxide film formation due to high solvation with water molecules. In such solutions, the kinetics are poor.

The kinetics are better in low dielectric constant solutions for 20%, 40%, 60% and 80% aquo-glycolic media, the dielectric constant values are low leading to a marked improvement in the kinetics.

### 5.2 SCANNING ELECTRON MICROGRAPHS:

Figure -3 and Figure - 4 are the Scanning Electron Micrographs of anodic films formed on Zr-Nb in aqueous and aquo-glycolic solutions of 0.1M EDTA (Sodium salt) upto 200V.

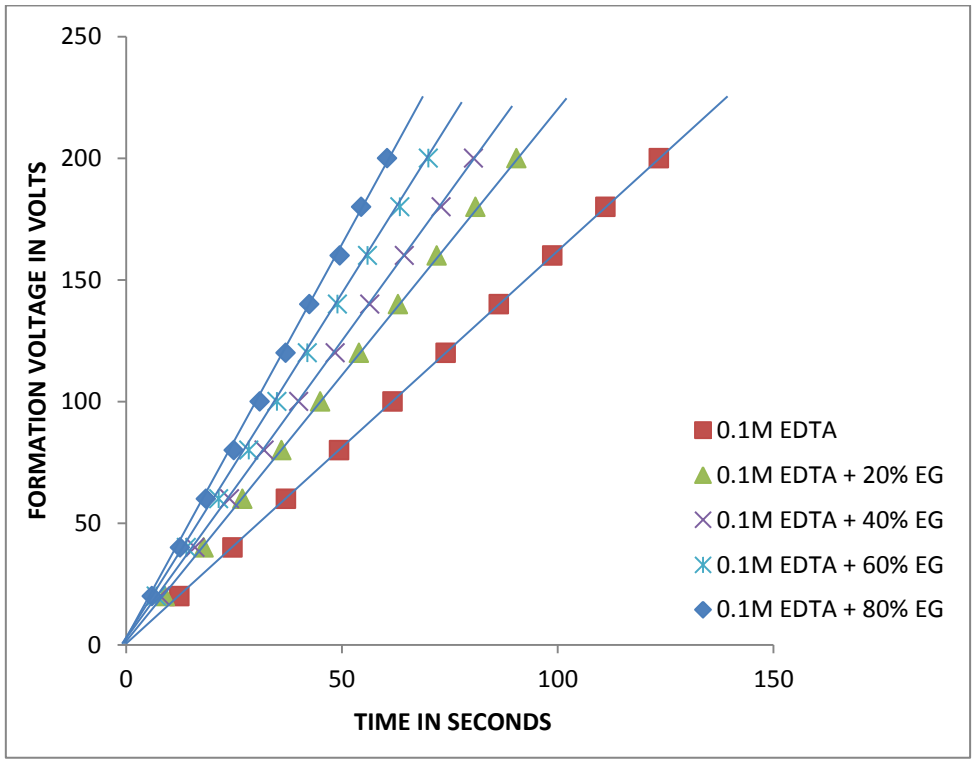


**Figure 1: Plot of formation voltage as a function of time in aquo-glycolic solution**

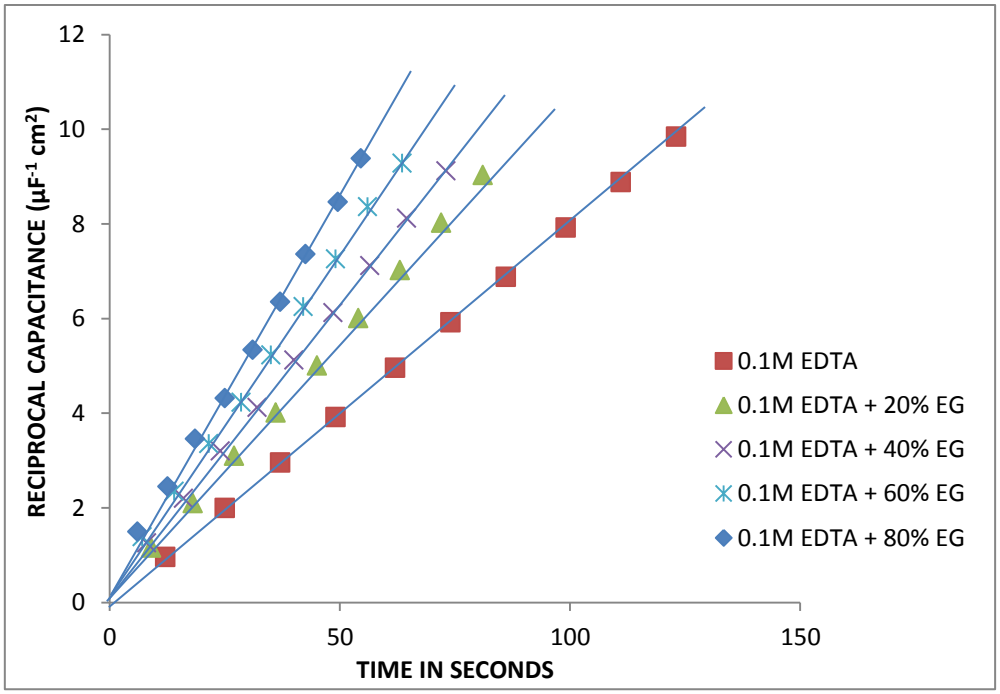


**Figure 2: Plot of reciprocal capacitance as a function of time in aquo-glycolic solution.**

**Table 1: Anodic films formed on Zr-Nb in 0.1M Ethylene Diammine Tetra Acetic Acid (sodium salt) both aqueous and aquo-glycolic media.**

| Electrolyte | Formation Rate, dV/dt ($V.s^{-1}$) | Current efficiency, η (%) | Differential field, $F_D$ ($MV.cm^{-1}$) |
|---|---|---|---|
| 0.1M EDTA | 1.61 | 77.1 | 4.680 |
| 0.1M EDTA + 20% EG | 1.72 | 81.5 | 4.584 |

| | | | |
|---|---|---|---|
| 0.1M EDTA + 40% EG | 1.78 | 86.4 | 4.539 |
| 0.1M EDTA + 60% EG | 1.82 | 88.0 | 4.523 |
| 0.1M EDTA + 80% EG | 1.88 | 91.5 | 4.475 |

EDTA-Ethylene Diamine Tetra Acetic acid EG-Ethylene glycol

Table 2: Variation of dielectric constant as a function of solution composition

| EG , % | 0 | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|
| Dielectric constant | 80.0 | 72.8 | 69.2 | 57.8 | 43.2 | 37.7 |

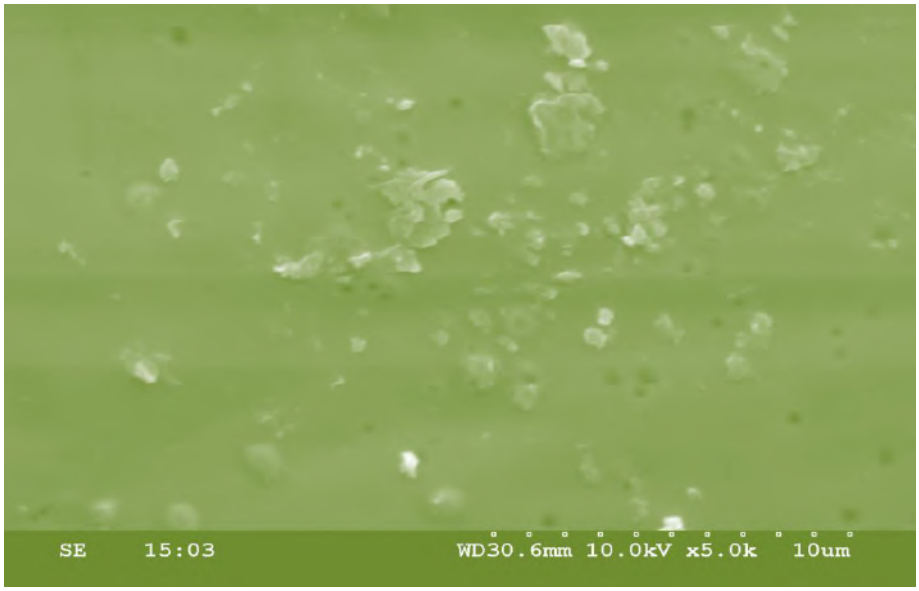


Figure 3: SEM of the film formed upto 220V in 0.1M EDTA (Sodium salt) (aqueous medium) at room temperature (Magnification of the micrograph is X 5000)

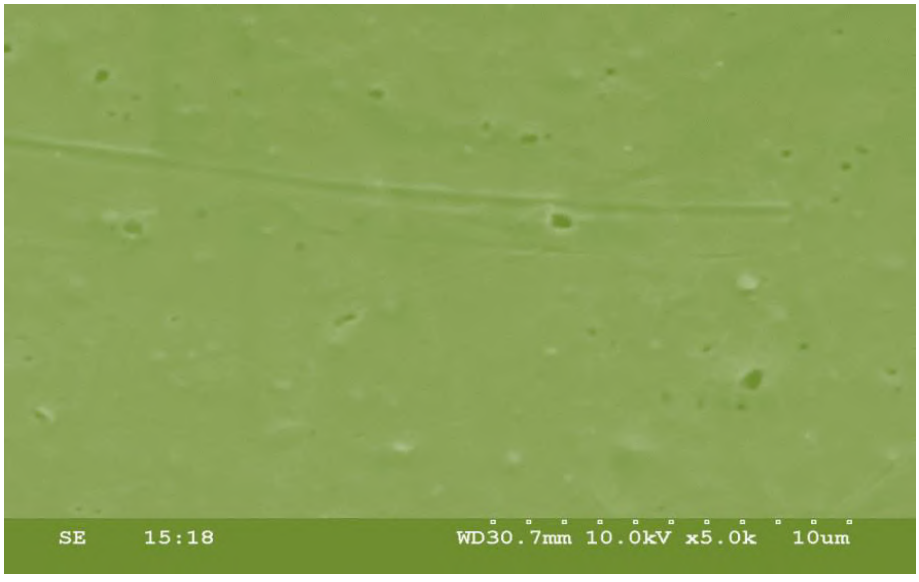


Figure 4: SEM of the film formed upto 220V in 0.1M EDTA (Sodium salt) (glycolic medium) at room temperature (Magnification of the micrograph is X 5000)

When compared, the roughness and non-uniformity of the surface are decreased when electrolytic medium is changed from aqueous to aquo-glycolic medium (fig-4) is observed to be smoother than the film formed in aqueous medium (fig-3).

**5.3 EFFECT OF TEMPERATURE:**

Anodizations were carried out on Zr-Nb at various temperatures ranging from 273K to 333K and at a constant current density of 8 $mA.cm^{-2}$. The conventional plots were drawn as shown in the Figures: 5 & 6. From these plots, the kinetic results were calculated. It was observed that the formation rate, current efficiency, differential field & break down voltage were found to be increasing linearly with the decrease in temperature as shown in Table-3.

The decrease in the field, formation rate & Breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

Colton & Wood [24] reported that the BDV was decreased with increase in temperature in the case of titanium oxide films and explained the observation on the basis of dissolution of the film.

Bhaskar reddy et al [25] observed the similar trend of decreasing kinetic results with increase in temperature in 0.1M potassium tartarate. The same results were observed by many others [26-31].

**TABLE 3: Anodic films formed on Zr-Nb in 0.1M 0.1M EDTA (Sodium salt) at different temperatures**

| Temperature ,T (K) | Formation rate,dV/dt ($V.s^{-1}$) | Current efficiency, η (%) | Differential field, $F_D$ ($MV.cm^{-1}$) | Break down voltage ($V_B$) , Volts |
|---|---|---|---|---|
| 273 | 2.70 | 90.0 | 5.840 | 238 |
| 288 | 2.10 | 67.0 | 5.720 | 210 |
| 303 | 1.72 | 62.0 | 5.628 | 201 |
| 318 | 1.64 | 58.5 | 5.540 | 177 |
| 333 | 1.29 | 48.2 | 5.310 | 149 |

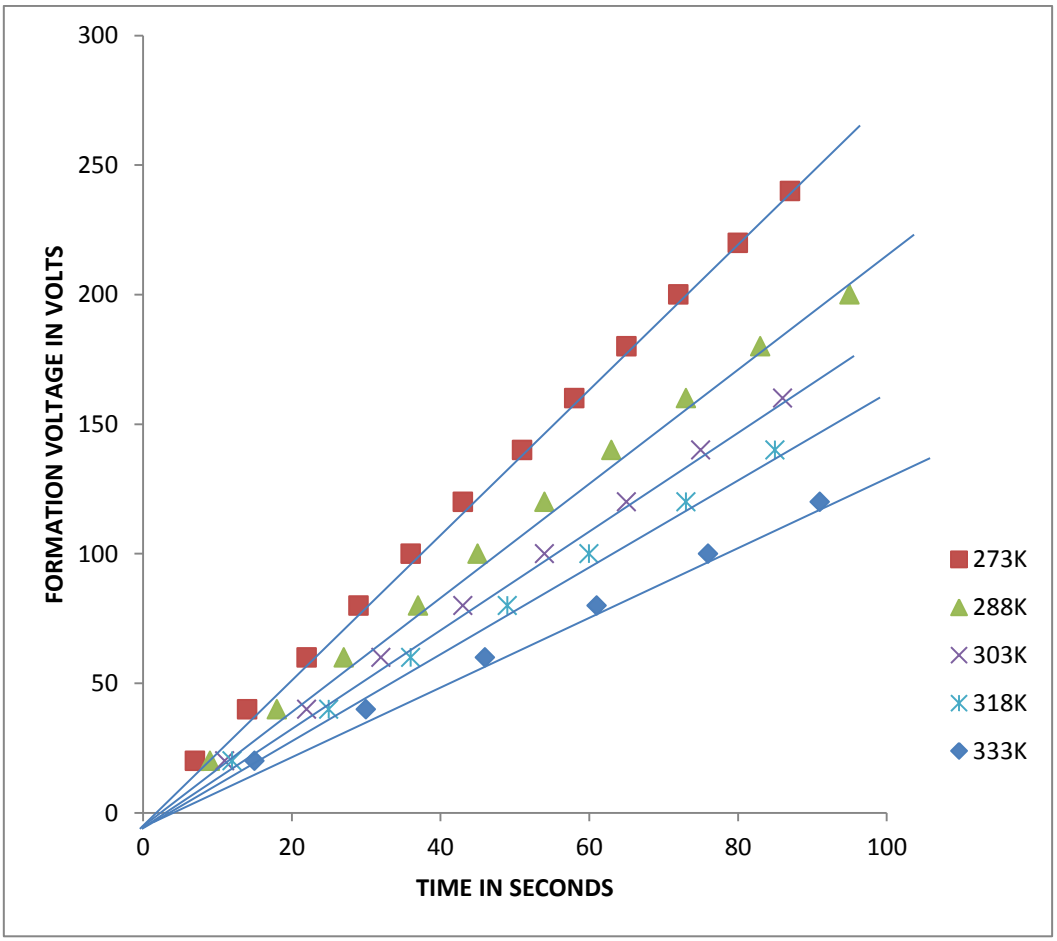


**Figure 5: Plot of formation voltage as a function of time at different temperatures.**

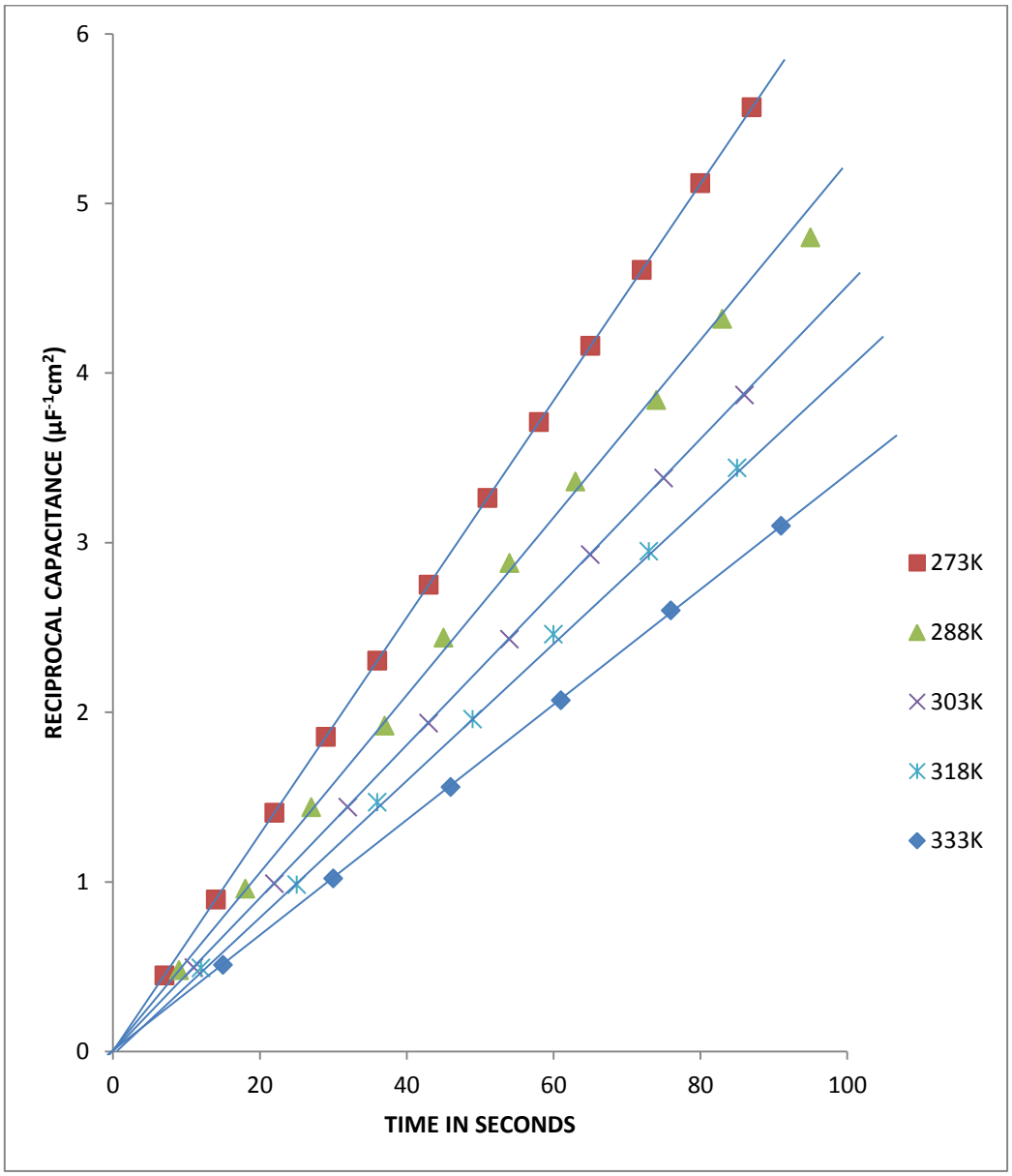


**Figure 6: Plot of Reciprocal Capacitance as a function of time at different temperatures.**

## 6. CONCLUSIONS:

By changing the solvent medium from aqueous to glycolic, the kinetics of film formation on Zr-Nb in 0.1M EDTA (Sodium salt) have been studied and it is observed that the peak voltage, formation rate, current efficiency are increased but differential field of formation decreased with the glycol content of solution. This can be attributed to the decrease in the dielectric constant of the solution with the increase in glycol content of the solution.

It was also observed that the kinetics were good at low temperatures. It was observed that the formation rate, current efficiency, differential field & break down voltage were found to be increasing linearly with the decrease in temperature. The decrease in the field, formation rate & breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

## 7. APPLICATIONS OF ANODIC OXIDE FILMS:

- Capacitors
- Diodes
- Semiconductors
- Resistors
- Photo chemical devices
- As a base for selective electroplating, painting & decorative purposes
- Nuclear technology (nuclear fuel storage & water cooled nuclear reactors)

- Electrolytic condensers
- Insulators
- Good corrosion resistant.

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**REFERENCES:**

1. Williams C D, (1969): *Atomic energy of Canada Limited Report*, AECL; 3456.
2. Williams C D, (1970) : *Reactor technol.,*; Vol-13, pp. 147.
3. Shobha Rani P, Anjaneyulu Ch and Sastry K S, (2000): *J. Electrochemical Soc India*, Vol.49, no.3, pp.129
4. Lavanya A and Anjaneyulu Ch, (2004): *Bull. Electrochem.*, Vol.20, no. 4, pp. 153
5. Lavanya A, Raghunath G and Anjaneyulu Ch, (2004): *Bull. Electrochem.,*; Vol. 20, no.7, pp. 305
6. Ashok Kumar V, Raghunath G and Anjaneyulu Ch, (2005): *Bull. Electrochem.,* Vol.21, no. 1,pp.17
7. D.A.Vermilyea,( 1953): *Acta Met.,*Vol. 1, pp. 282
8. D.A.Vermilyea,( 1954): *Acta Met.,*Vol. 2,pp. 482
9. I.E.Seregina, B.Kopara and A.V.Thimoshenko, (1982): Deposited Doc. *(Avail SPSTl),* no.10
10. B.Nageshwar Rao.V.Venkata Ramana & Ch.Anjaneyulu, ( 1996): *J.Electrochem.Soc.India*, Vol.45, no.27
11. N.N.S.Aparna, (2009): *Ph.D.Thesis*, O.U.
12. Mashashi Koyama, (1962): Rikagaku Kemyusho Hokoku, Vol.38, no.321, pp.546.
13. Wei Wei, Jan M.Macak, Nabeen, K.Shreshta & Patrick Schmuki, (2009): *J.Electrochem.Soc.,*;Vol.156, pp. K104-K109.
14. HK Schmidt, R.Capellodes & M.I.Vidal, M.T Vida, Lab. Invest. Components, Electron.S.A, (1982): *Fr. Rev. Tech. Thomson C.S.F.*, Vol. 14, pp.657 (FR)
15. F.Climent Montaliu, R.Fart Capellodes & M.I.Vidal, (1983): *Plennels An. Quim. Ser.B.,* Vol.79, pp.290
16. A.Panasa Reddy, Ch.Anjaneyulu & K.S.Sastry, (1990): *J.Electrochem.Soc.India*., Vol. 39,pp.183.
17. A.Lavanya, C.S.N.Sarma & Ch.Anjaneyulu, (2001): *J.Electrochem.Soc.India*, Vol. 50,pp. 164.
18. A.Panasa Reddy, A.N.Chary, Ch.Anjaneyulu & K.S.Sastry, (1984): *J.Electrochem.Soc India.,* Vol.33,pp. 229
19. V D Shukla and Anjaneyulu Ch, (2011): *E-Journal of Chemsistry,* Vol. 8,no. 1, pp.71-76.
20. Lavanya A and Anjaneyulu Ch, (2002): *Bull. Electrochem.,*Vol. 18, pp.317
21. Arifuku F, Iwakura C, Yoneyama H and Tamura H, (1978): Denki Kagaski, Vol.46, pp.19
22. Randal J, (1975): J, *Electrochim Acta,* Vol.20, pp. 663
23. Lavanya A, Sarma C S N and Anjaneyulu Ch, (2001): *J Electrochem Soc India*, Vol.50, pp.164
24. JB Colton., (1963): Trans Int Chem Engg., Vol. 41, pp. 11.
25. P Bhaskar Reddy, A Panasa Reddy, (2003): Bull Electrochem., Vol.19, no.11, pp. 481-482.
26. SS Abdel Rehim, HH Hassan, MA Amin., (2002): J Applied Electrochem Vol.32, pp.1257-1264.
27. Ch Anjaneyulu and KS Sastry.( 1981): J Applied Electrochem., Vol. 30, pp.282.
28. A Panasa Reddy, Ch Anjaneyulu and KS Sastry, ( 1990): J Electrochem Soc India, Vol.39, pp.183.
29. A Panasa Reddy, AN Chary, Ch Anjaneyulu and KS Sastry. (1984): J Electrochem Soc India Vol.33, pp. 229.
30. JE Norman, (1977): Corros. Sci., Vol. 17, pp. 39.
31. NP Tomashov, Chin-Min Shih and FP Zalivalon.,( 1963): Zh Prikl Khim, Vol. 36, pp. 1503.